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14. ABSTRACT
Our work for the AFOSR has three primary components:

Development of new quantum theory for the accurate description of molecular structure and spectra.

Implementation of this new theory into general purpose computer programs (ACES II and pralel ACES III) to make it possible for many investigators, besides ourselves, to readily apply these new methods to problems of their interest.

Application of these new methods to challenging molecules chosen to test the new methods, and to other systems of interest to AFOSR. These include high energy, density molecules, where the new methods allow an assessment of their energy content, stability, possible synthetic paths, activation barriers, and provide spectroscopic fingerprints for identification. We also make applications of interesting clusters, atmospheric systems, potentital interstellar molecules, and to gas phase molecular reactions of the sort that can occur in flames.

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FINAL TECHNICAL REPORT

University of Florida

GRANT # fa9550-04-1-0119

TITLE: METASTABLE MOLECULES IN THE GROUND AN
IN EXCITED STATES,THEORY DEVELOPMENT,
IMPLEMENTATION AND APPLICATION

From: 01/01/2006 ended 12/31/2006

By: Dr. R J Bartlett

To: technicalreports@afosr.mil
Subject: Final Technical Report to Dr. Michael Berman

Contract/Grant Title: Metastable Molecules in Ground and Excited States and their Description with New Quantum Mechanical Methods

Contract/Grant #: FA9550-04-1-0119

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I.   Objectives

Our work for the AFOSR has three primary components:

- Development of new quantum theory for the accurate description of molecular structure and spectra

- Implementation of this new theory into general purpose computer programs (ACES II and pralel ACES III) to make it possible for many investigators, besides ourselves, to readily apply these new methods to problems of their interest

- Application of these new methods to challenging molecules chosen to test the new methods, and to other systems of interest to AFOSR. These include high energy, density molecules, where the new methods allow an assessment of their energy content, stability, possible synthetic paths, activation barriers, and provide spectroscopic fingerprints for identification. We also make applications ot interesting clusters, atmospheric systems, potential interstellar molecules, and to gas phase molecular reactions of the sort that can occur in flames.

Section II summarizes some of the highlights of our work for the past year. The references refer exclusively to the recent papers published under this grant, listed in Section III. Section IV shows the invited presentations assisted by this grant. Sections V and VI reports the students and postdocs supported under this work. Section VII lists the several honors that accrued during this reporting period.

II. Accomplishments:

A. We have shown in a series of papers [3,5,7,8], that we are able to use explicit orbital dependent functionals of the energy obtained from MBPT or CC theory to construct proper exchange-correlation potentials in density

functional theory. In this way, we obtain the correct behavior of the potential as a function of r, unlike any of the standard local, gradient corrected, or hybrid procedures. A comparison of our OEP2 correlation potential and the PBE gradient corrected correlation potential is shown in the following figure:
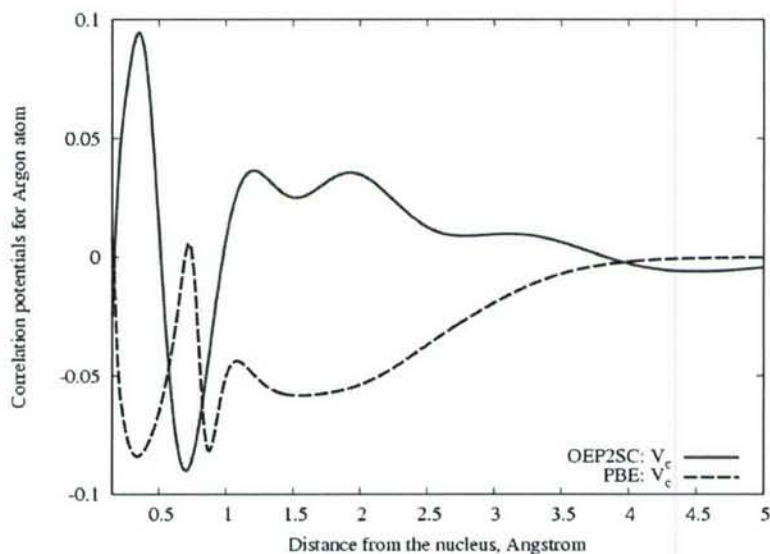

B. For 35 molecules we show how such correct potentials affect the numerical results for energies compared to ab initio and standard DFT

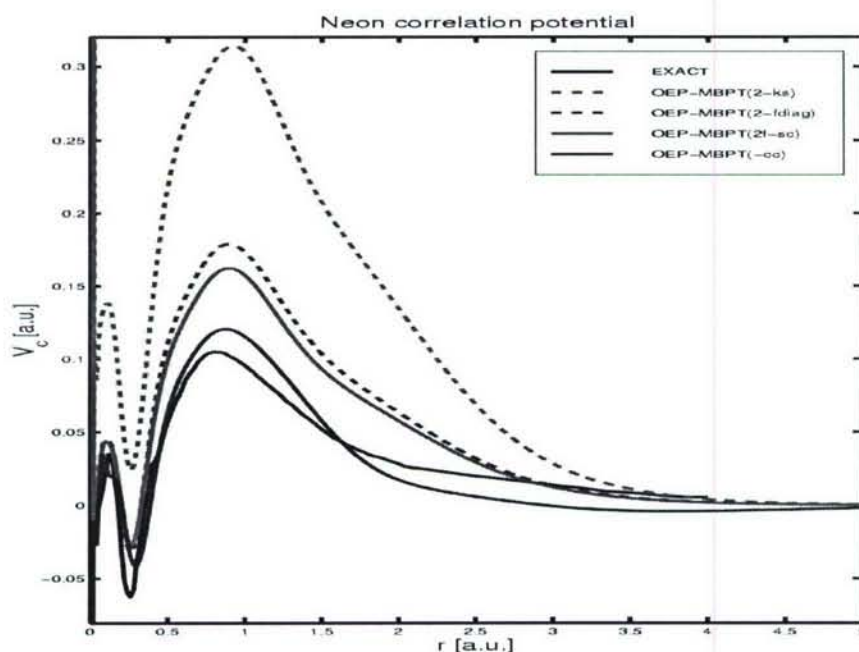methods.

Relative deviation
from CCSDT energy
(35 systems)

C. Aided by having the correct potentials, we obtain much improved
energies, ionization potentials, and related properties from our *ab initio dft*
calculations. In particular, we properly obtain weak (Van der Waals)
interactions that cannot be described with standard dft methods. This is

illustrated for Ne_2 and Ar_2:

Ne dimer potential energy

Ar2
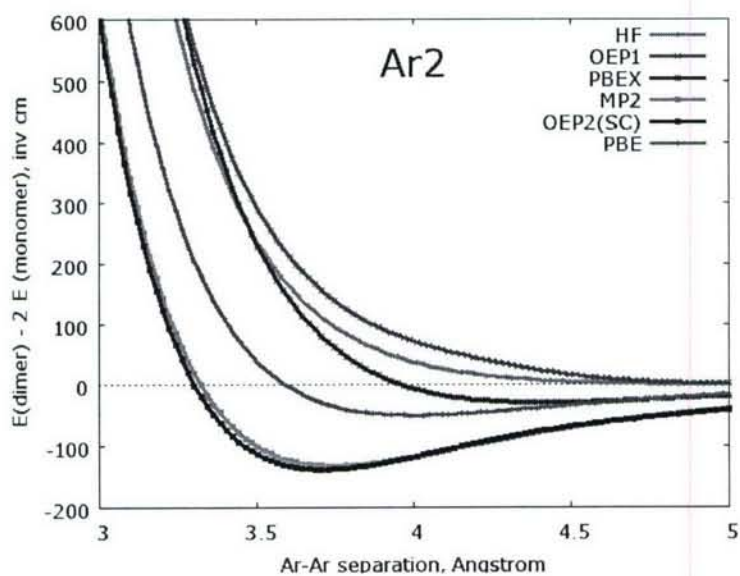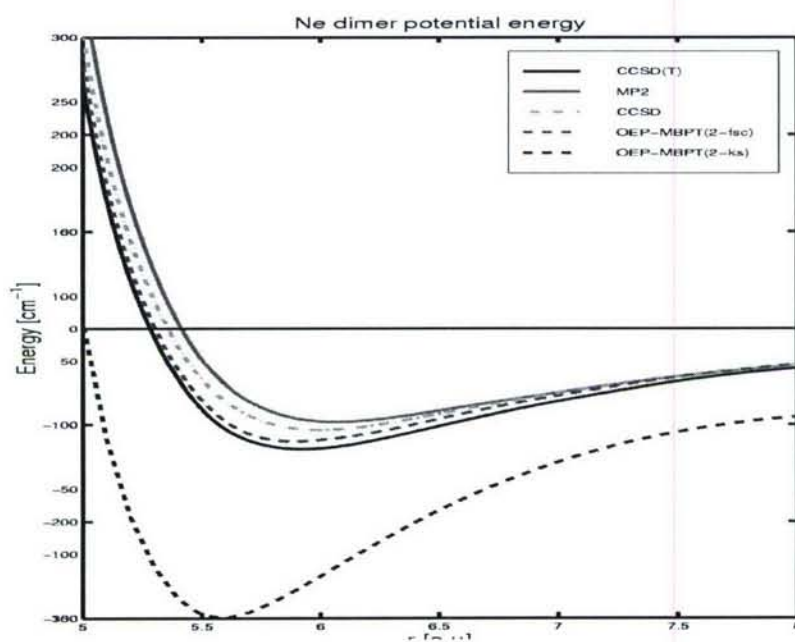
D. We have recently generalized our procedure to use some infinite-order summations like those of coupled-cluster theory, to demonstrate that even better results can be obtained than by the generalized second-order

based OEP2 method shown above. We also demonstrate that use of the Kohn-Sham orbital energies in the denominators of these equations causing unphysical convergence difficulties, and in particular, give much too low total energies when it does converge. On the other hand, our approach that uses semi-canonical transformations to provide properly invariant, second-order perturbation theory, behaves very well making it a computationally attractive method.

Neon correlation potential

E. In coupled-cluster (CC) theory our primary focus this past year was the new hierarchy of CC methods we introduced called nCC.[21].The 'n' means these are the minimum CC methods that are correct for n electrons. As such, they are less time-consuming to compute than the usual CCSD, CCSDT, and CCSDTQ methods, since making them correct for n-electrons means that many of the most time consuming contributions from non-linear terms in CC can be neglected. For example, nCCSD provides the exact result for 2 electrons, and all products of 2-electron units. Yet, it scales computationally as $\sim N^2$, where N is the number of virtual orbitals in a calculation, while the rest of the non-linear terms in the full CCSD scale as $\sim N^3$. Even greater gains are possible for nCCSDT and nCCSDTQ. Yet in all cases, the method is fully size-extensive, has the same orbital invariance and insensitivity as the full CC method, and has to give the exact results, just as the full methods, would, for 2,3,4, …electrons.

F. The new nCC hierarchy also suggests better ways to ensure correct separation of a molecule to its fragments. Since for separated pairs of electrons, nCCSD has to give the correct answer, it follows that a four

electron system separating into two, two-electron systems has to go to nCCSD in the limit, even though for the full four electron problem, nCCSDTQ would be necessary to get the exact answer away from the limit. This feature is being studied currently in the separation of ethylene to two methylenes, and N_2 to two three electron (out of a closed shell) problems. Finally, combining nCC with our new natural linear scaled CC method (discussed below), we expect to be able to separate the correlation problem into physically meaningful 2, 3, and 4 electron units for very large molecules.

G. Because of nCCSD being exact for two electrons, and all products of two electrons, it is the natural zeroth-order approximation for the separated electron pair bonds in chemistry. Furthermore, the transition from CCSD to nCCSD eliminates the most time-consumng steps in the evaluation of the non-linear terms in CCSD. Nonetheless, the method is exact for two electrons, and all products of two electrons as it is still composed solely of linked diagrams as required by its extensivity. Furthermore, it still retains all the invariance properties of CCSD, meaning that it is invariant to transformations among just occupied or virtual orbitals. This distinguishes this method from CEPA-like approximations (ie coupled electron pair approximations) that are not invariant to orbital rotations. Finally, nCCSD has the same orbital insensitivity as does CCSD, since the $\exp(T_1)$ operator is not truncated.

H. The QCISD method of Pople had the property that it was exact for two-electrons, but 2CC is an simpler and faster computational approximation that satisfies the same criteria. Also, whereas QCISD could not be generalized to triple excitations and higher, and thereby could not satisfy the exactness condition for 3 and 4 electrons, 3CC and 4CC do exactly that, and if desired, could even be extended to higher excitations. QCISD also truncated the $\exp(T_1)$ rather severely, so any kind of sensitive one-electron property could be off by orders of magnitude, as we showed for the IR vibrational intensity and polarizability of BeO.

I. The secret of the nCC theory is to retain the so-called occupied-occupied(EPV) or hole-conjoint (HCJ) diagrams that are required to get exact results for 2 ,3, 4, ... electrons, but do not retain any other non-linear diagrams that are not necessary to fulfil that requirement. At the CCD level, ie in the absence of single excitations, the non-HCJ diagrams are precisely those that would be excluded in the ACCD method of Dykstra or the D(4,5) approximation of Paldus. The motive in the first case, was to simplify the CCD calculation, and in the second, to potentially benefit from some mutual cancellations with connected quadruples in exactly soluble model problems. Their exclusion in nCCSD has a substantially different rationale, but will still benefit from the latter aspect, as well.

J. A few results are shown for water and ethylene for the nCC methods versus the full CC ones, in the following. These show the accuracy of nCC for energies, and associated potential energy curves.

Total energies E (in Hartrees) of the H_2O molecule[a]
(DZP basis set: $R_{OH}=R_e=0.956$ Å, $\angle 105.2°$)

	R_e	$1.5R_e$	$2.0R_e$	$2.5R_e$
CCSDTQ	-76.259351	-76.097040	-75.965094	-75.926362
nCCSDTQ	-76.259344	-76.097009	-75.964969	-75.925680
CCSDT	-76.258905	-76.095570	-75.965254	-75.946782
nCCSDT	-76.258869	-76.095493	-75.965038	-75.946435
CCSD	-76.255409	-76.088106	-75.945326	-75.905020
nCCSD	-76.253132	-76.085209	-75.945926	-

[a] 8 electrons were correlated.

$$\text{nCCSDTQ-CCSDTQ} < 0.1 \text{ mH}$$
$$\text{nCCSDT-CCSDT} < 0.3 \text{ mH}$$
$$\text{nCCSD-CCSD} < 3 \text{ mH}$$

Remember, for 4 electron ethylene CC-nCC results $\cong 0$.

Ethylene with 12 electrons correlated (DZP)

	R_{eq}	∞
CCSDTQ-nCCSDTQ	1×10^{-5}	$< 10^{-5}$
CCSDT-nCCSDT	8×10^{-5}	$< 10^{-5}$
CCSD-nCCSD	2×10^{-3}	$< 10^{-4}$
CCSDTQ-CISDTQ	2.3×10^{-3}	2×10^{-4}
CCSDT-CISDT	2.6×10^{-2}	6×10^{-3}
CCSD-CISD	2.4×10^{-2}	5×10^{-3}

Much greater errors are introduced in the CI methods for 12 electrons compared to their CC counterparts. This is a manifestation of size-inextensivity of CI.

K. A similar accuracy is also possible for excitation energies, using the nCC solution for the ground state, as in the next table.

Verical excitation energies (eV) of the N_2, CO, C_2, and H_2O molecules in POL1 basis set.[a]

| Mol.	Sym.	EOM-CCSD	EOM-CCSDT	EOM-nCCSD	Exp.
N_2	$^1\Pi_g$	9.600	9.519	9.554	9.31
	$^1\Sigma_u^-$	10.308	10.165	10.265	9.92
	$^1\Delta_u$	10.726	10.549	10.667	10.27
CO	$^1\Pi$	8.764	8.664	8.745	8.51
	$^1\Sigma^-$	10.193	10.162	10.141	9.88
	$^1\Delta$	10.314	10.285	10.257	10.23
C_2	$^1\Pi_u$	1.425	1.361	1.525	1.041
	$^1\Sigma_u^+$	5.772	5.678	5.872	5.361
H_2O	$^1B_1$	7.400	7.460	7.359	7.4
	$^1A_2$	9.156	9.228	9.114	9.1
	$^1A_1$	9.823	9.876	9.785	9.7

[a] Valence electrons correlated.

L. The natural linear scaling coupled-cluster method (NLSCC) we have recently introduced[2] uses molecular units, properly terminated by H atoms, and described by localized bond orbitals. The latter are the natural localized molecular orbitals proposed by Weinhold. Using them, we show that all integrals and CC amplitudes fall off as r^{-3}, which permits the accurate CC solution of quite large systems like polyglycine. We use overlapping neighborhoods that extend beyond the molecular unit itself. We also have exceptional transferability as the amplitudes so defined reflect much of the well-known chemical properties that chemical bonds tend to be similar in different molecules. Also, unlike other types of localized orbital methods built upon atomic orbitals or their projections relative to a set of local MO's; all of our functions are orthogonal molecular orbitals, making the calculations much more efficient. In the last year, we have explored the role of triple excitations in NLSCC and in using NLSCC for excited states of large molecules.

Example : CCSD Correlation Energy of Polyglycine (GLY)$_x$

Dangling bonds of QM2 boxes terminated by H atoms

A   B

C   D
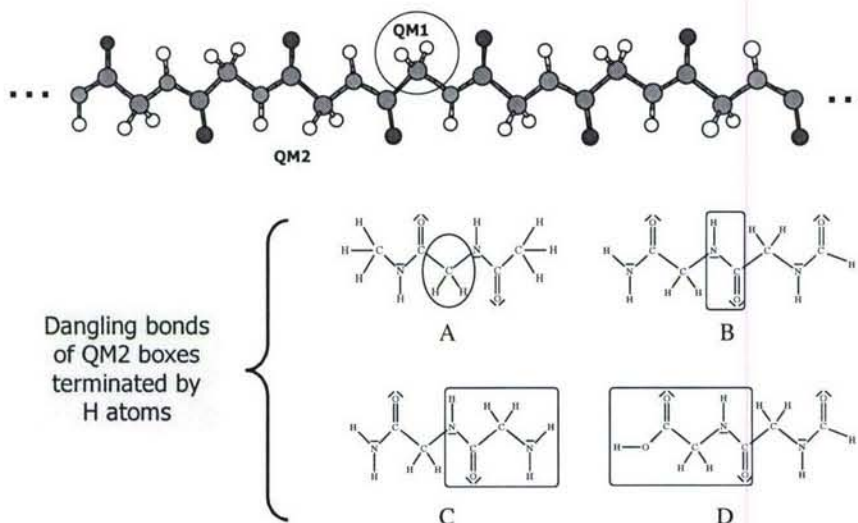
Results

NLMO CCSD orbital correlation energies (cc-pVDZ) from QM2 box C:

C
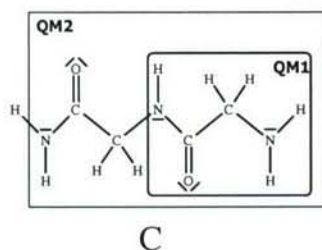
i	ΔE_i (H)
C-H (methylene,2x)	−.0480
C-C (methylene)	−.0527
C-N (methylene)	−.0564
L.P. N (peptide)	−.0643
L.P. O (peptide)	−.0484
L.P. O (peptide)	−.0615
N-H (peptide)	−.0525
C-N (peptide)	−.0527
σ C-O (peptide)	−.0495
π C-O (peptide)	−.0746
L.P. N (amino)	−.0534
N-H (amino,2x)	−.0521

M. These two figures show that a potentially infinite polymer like polyglycine can be decomposed into two quantum mechanical regions and a third region. QM1 Is the target functional group that is to be determined within the QM2 region as a large molecule calculation. Then QM1 Is expected to be correctly described from coupled-cluster theory and transfearable. So after determination of the various units, seen in the lower figure, there is a correlation energy associated with each local bond. Once these are known, then the correlation energy in any number of

units of polyglycine can be obtained from simply adding them up. Current work deals with the same kind of transferablility for the densities and polarizabilities.

III. Publications (Sept. 2004-present, supported by AFOSR).

Journals

1. T. Henderson and R. J. Bartlett, "Short-range corrections to the correlation hole," Phys. Rev. A **70**, 022512 (2004).
2. N. Flocke and R.J. Bartlett, "A natural linear scaling coupled-cluster method," J. Chem. Phys. **121**, 10935 (2004).
3. R. J. Bartlett, I. Grabowski, S. Hirata, and S. Ivanov, "The exchange-correlation potential in *ab initio* density functional theory, J. Chem. Phys. **122**, 034104 (2005).
4. S. Hirata, S. Ivanov, R.J. Bartlett and I Grabowski, "Exact-exchange time-dependent density functional theory for static and dynamic polarizabilities," Phys. Rev. A **71**, 032507 (2005).
5. V. Lotrich, R.J. Bartlett and I Grabowski, "Intramolecular potential energy surfaces computed from DFT: The right answer for the right reason," Chem. Phys. Letts. **405**, 43-48 (2005).
6. R. J. Bartlett, I. Grabowski, S. Hirata, and S. Ivanov, The Exchange-Correlation Potential in Ab Initio Density Functional Theory, J. Chem. Phys. **122**, 034104 (2005).
7. R. J. Bartlett, V. F. Lotrich, I.V. Schweigert, "*Ab Initio dft*: The Best of Both Worlds?" J. Chem. Phys. **123,** 062205 (2005)
8. T. Henderson and R.J. Bartlett, "Theory of the short-range correlation hole model," Mol. Phys. **103,** 2093 (2005),
9. D. Bokhan, I. V. Schweigert and R.J. Bartlett, "Interconnection between functional derivative and effective operator approaches to ab initio density functional theory", Mol. Phys.**103**, 2299 (2005),
10. S. A. Perera, P. Rozyczko, S. Hirata and R.J. Bartlett, "Improving the performance of direct coupled energy and gradient calculations, Mol. Phys.**103**, 2081 (2005)
11. M. Musial, L. Meissner, S. A. Kucharski and R. J. Bartlett, "Molecular Applications of the Intermediate Hamiltonian Fock-Space Coupled-cluster Method for Calculation of Excitation Energies," J. Chem. Phys. **122**, 224110 (2005).
12. M. Musial and R. J. Bartlett, "Critical Comparison of Various Connected Quadruple Excitation Approximations in the Coupled-cluster Treatment of Bond Breaking," J. Chem. Phys. **122**, 224102 (2005).
13. D. Bokhan and R. J. Bartlett, "Adiabatic *Ab Initio* Time-dependent density functional theory employing optimized-effective-potential many-body perturbation theory potentials," Phys. Rev. A **73,** 022502 (2006).
14. R.J. Bartlett, I. Schweigert and V. Lotrich, "Getting the right answer for the right reason," Proceedings of the WATOC Plenary Sessions, J. Mol. Struct.: THEOCHEM **771**, 1-8 (2006).

15. D. Bokhan and R.J. Bartlett, "Ab initio density functional theory for spin-polarized systems," Chem. Phys. Lett. **427**, 466-471 (2006).
16. S. Ajith Perera and R.J. Bartlett, "Hidden symmetry in Fermi-contact NMR spin-spin coupling constants," Mol. Phys. **104**, 2403-2411 (2006).
17. R.J. Bartlett, I. Schweigert, and V. Lotrich, "Ab initio DFT: Getting the right answer for the right reason," Proceedings of the WATOC Plenary Sessions, J. Mol. Struct. (THEOCHEM) **771**, 1-8 (2006).
18. M. Musial, K. Kowalska, and R.J. Bartlett, "Accurate calculation of vibrational frequencies in excited states with the full EOM-CCSDT method," J. Mol. Struct. (THEOCHEM) **768,** 103-109 (2006).
19. A. Taube and R.J. Bartlett, "New perspectives on unitary coupled-cluster theory," Int. J. Quantum Chem. **106,** 3393-3401, (2006).
20. I. V. Schweigert, V. F. Lotrich and R. J. Bartlett, "*Ab initio* correlation functionals from second-order perturbation theory," J. Chem. Phys. **125** 104108 (2006).
21. R.J. Bartlett and M. Musial, "Addition by subtraction in coupled-cluster theory: A reconsideration of the couple cluster and CI interface and the *n*CC hierarchy," J. Chem. Phys.**125**, 204105 (2006).
22. R.J. Bartlett and M. Musial, "Coupled-cluster theory in quantum chemistry", Revs. of Modern Phys. **79,** 291-352 (2007).

Chapters

1. M. Musial, S.A. Kucharski and R.J. Bartlett, "Approximate inclusion of the T_3 and R_3 operators in the equation-of-motion coupled cluster method," in *Advances in Quantum Chemistry*, Volume 47, Academic Press, 209-221 (2005)

2. S.A. Perera and R.J. Bartlett, "A Reinvestigation of Ramsey's Theory of NMR Coupling," in *Advances in Quantum Chemistry*, Academic Press, 435-467 (2005).

3. R. J. Bartlett, "How and Why Coupled-cluster Theory Became the Pre-eminent Method in *Ab Initio* Quantum Chemistry?" in *Theory and Applications of Computational Chemistry: The First Forty Years,* (C. Dykstra, G. Frenking, K. Kim and G. Scuseria, editors) Elsevier, 1191-1221 (2005).

IV. Invited Lectures at Professional Conferences (Sept. 2004 to the present, supported by AFOSR).

July 2006 – "Progress in Ab Initio DFT," 6th Canadian Computational Chemistry Conference, Vancouver, Canada

June 2006 – "Addition by Subtraction in Coupled-Cluster Theory: The nCC Hierarchy," Canadian Society for Chemistry, Halifax, Nova Scotia

May 2006 – "Addition by Subtraction in Coupled-Theory: A Reconsideration of the Coupled-Cluster/CI Interface," Chemical Accuracy and Beyond, Satellite Meeting of the XIIth Congress of the International Academy of Quantum Molecular Sciences, Tokyo, Japan

March 2006 – "Ab Initio Density Functional Theory: The Seamless Connection with Wavefunction Theory," ACS Meeting on Honor of Robert G. Parr, Atlanta, GA

September 2005 – "Progress and Problems in ab initio DFT for Ground and Excited States," 11th International Conference on the Applications of Density Functional Theory in Chemistry and Physics, Geneva, Switzerland

October 2005 – "Electronic Structure of Molecules and Materials: From Coupled-Cluster Theory to DFT to the Transfer Hamiltonian," International Conference of Computational Methods in Sciences and Engineering, Loutraki, GreeceAugust 2005, "Energy Landscapes and Advances in Coupled-Cluster Theory."

August, 2005, "Energy Landscapes and Advances in Coupled-Cluster Theory," Fall ACS 230th National Meeting, Washington, DC

August 2005, Symposium in Honor of W. N. Lipscomb, Shanghai, CHINA.

July 2005, Fifth Congress of the International Society of Theoretical Chemical Physics, New Orleans, LA.

June 2005, "CECAM Workshop on Weak Interactions in Density Functional Theory," Lyon, France.

March 2005 – J. Pople Memorial Symposium, ACS 229th Spring National Meeting, San Diego, CA

January 2005 – Computational Tools for Molecules, Clusters, and Nanostructures: A Meeting in Honor of Reinhardt Ahlrichs, Karlsruhe, Germany

January 2005 – Fifth Congress of the World Association of Theoretically Oriented Chemists, Cape Town, South Africa

December 2004 – Consortial Workshop on Computational Physics 2004, Hsinchu, Taipei, Taiwan

Sept 2004 – Electronic Structure: Principles and Applications (ESPA-2004), Valladolid, Spain

V. Students graduated.

In 2004 we had four students graduate with their Ph. D. degrees:
Dr. Thom Henderson, now a postdoc at the University of Texas,.
Dr. Ariana Beste, now a postdoc at Oak Ridge National Laboratory.
Dr. DeCarlos Taylor, now an NRC postdoc at the Army Research Laboratory.
Dr. Anthony Yau, now a staff scientist at HPTi, Aberdeen, MD.

In 2005, Dr. Igor Schweigert received his Ph. D. He is now a postdoc with Shaul Mukamel, Univ. California, Irivine.
Densi Bokhan will graduate this summer, 2007.

VI. Other Students and Postdoctoral Associates.

There are currently six graduate students, Mr. Tom Hughes, Mr. Andrew Taube (DOD Fellowship), Mr. Denis Bokhan, Mr. Josh McClellan, Mr. Parkash Verma, and Ms. Anna Melichuk.

Also supported partly are Dr. Monika Musial, Dr. Victor Lotrich,   Dr. Norbert Flocke. Dr. Takashi Tschuiya, and Dr. Tomacz Kus

VII. HONORS

A special issue of Molecular Physics, vol. 103, numbers 15 and 16 was published in August 2005, that commemorates the 60th birthday of R. J. Bartlett. It constitutes the Proceedings of the St. Simons meeting entitled, "The Systematic Treatment of Electron Correlation", held in April 2004. The Proceedings consist of 34 papers, mostly written by prior and current members of the Bartlett group.

Recipient of ACS award in Theoretical Chemistry, 2007.

Recipient of the Shrödinger Medal from WATOC (World Association of Theoretical and Computational Chemistry) ,2008.

Changes in research objectives, if any: None

Change in AFOSR program manager, if any: None

Extensions granted or milestones slipped, if any: None